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DIFFERENTIAL THERMAL ANALYSIS STUDIES OF SOME SOIL-CLAYS FROM THE EASTERN CARIBBEAN, WEST INDIES. PART III. DOMINICA, TRINIDAD AND ST. VINCENT (MICACEOUS/MIXED MINERALS)

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ABSTRACT

DTA results were obtained for selected "micaceous" soil/clays from the Eastern Caribbean over the temperature range 300—1400 K. The thermograms run under N_2 were used to identify the clay minerals present. Supporting evidence on the clay minerals present was found from X-ray crystallographic techniques [1]. There is a marked similarity between the thermograms of the virgin soils analyzed under nitrogen gas and the clays from which the organic constituents had been analytically degraded.

INTRODUCTION

This study represents Part III of a continuing research program to fill the gap between DTA studies on West Indian soils and the extensive studies done on soil and clay minerals from most regions in the world. The differential thermal analytical (DTA) method of analysis has several advantages. It provides a simple, rapid and sensitive method and specificity for some mineral species which are not readily differentiated by diffraction properties. Differences in the temperature of hydroxyl-water loss provide a means of differentiating mineral species within any isomorphous series of minerals, since the mineral species is largely defined according to the nature of the isomorphously substituted structural ions.

This paper discusses the application in the study of clay mineralogy of micaceous West Indian soils. Illites are ill-defined crystals. They have a lower K_2O and higher H_2O content and cation exchange capacity than the micas. They are therefore considered as micas high in H_3O^+ [2,3] or H_2O [4]. The presence of randomly interstratified montmorillonite layers or of mica crystals with frayed and somewhat expanded crystal edges are possible [5,6]. Further, some may represent epitactic intergrowths of mica and kaolinite or even intergrowths of several other species [7,8]. However, DTA characteristics of illite are fairly well defined — i.e. low to medium temperature dehydroxylation endotherms and an S-shaped endothermic—exothermic system at ca. 900°C of which the exothermic section may represent formation of a spinel.

TABLE 1

Clay minerals (%) of selected West Indian soils

Soil	Origin	Mica	Others [a]
Barataria	Trinidad	45 ± 5(B) 25 ± 5(I)	Tr-(K), (F), and (Q)
Cunupia	Trinidad	20(I)	35 ± 5(K); 25 ± 5(M); 5(V); 5(Go); Tr(Q)
La Plaine	Dominica	35 ± 5(A); Tr(I)	45 ± 5(K); 6(Go); Tr(V); (C—V)
Montreal	St. Vincent	85 ± 5(B); 15 ± 5(A)	Tr-(M), (K), (F) and (V)
River Estate	Trinidad	50 ± 5(I)	25 ± 5(K); 8(Go); 4(M); (C—V); Tr(Q)
St. Augustine	Trinidad	25 ± 5(I)	Q; Tr-(C), (K) and (V)
Talparo	Trinidad	25 ± 5(I)	35 ± 5(K); 25 ± 5(M); 4(Go); (Q)

[a] A = allophane; B = biotite; C = chlorite; F = feldspar; Go = goethite; I = illite; K = kaolinite; M = montmorillonite; Q = quartz; V = Vermiculite; Tr = traces of.

EXPERIMENTAL

The sample preparations are as outlined in Parts I and II [9]. The same methods, apparatus and techniques were adopted. The soils used in this work are from the named areas of the Caribbean given in Table 1.

RESULTS AND DISCUSSIONS

General

The clays studied contain micas (biotite and illite), allophane, and mixed minerals (kaolinite, montmorillonite, vermiculite, chlorite, quartz and feldspar) either as monomineralic entities or interstratified species.

The DTA patterns of the "untreated" soils run in air all show a large low temperature exothermic reaction peak. The data of a representative sample, River Estate, of these soils are listed in Table 2 and illustrated in Fig. 1(1).

TABLE 2

DTA reaction temperatures of River Estate soil-clays

Condition	Temp. (°C)(E/X) [a]
Untreated; air	331(X); 528, 580(E)
Mg-Saturated; air	114(E); 237, 285, 532, (E); 621(E)
Untreated; N_2	83, 275, 504, 573(E)
Mg-Saturated; N_2	95, 205, 260, 520 and 577(E)

[a] E = endotherm; X = exotherm.

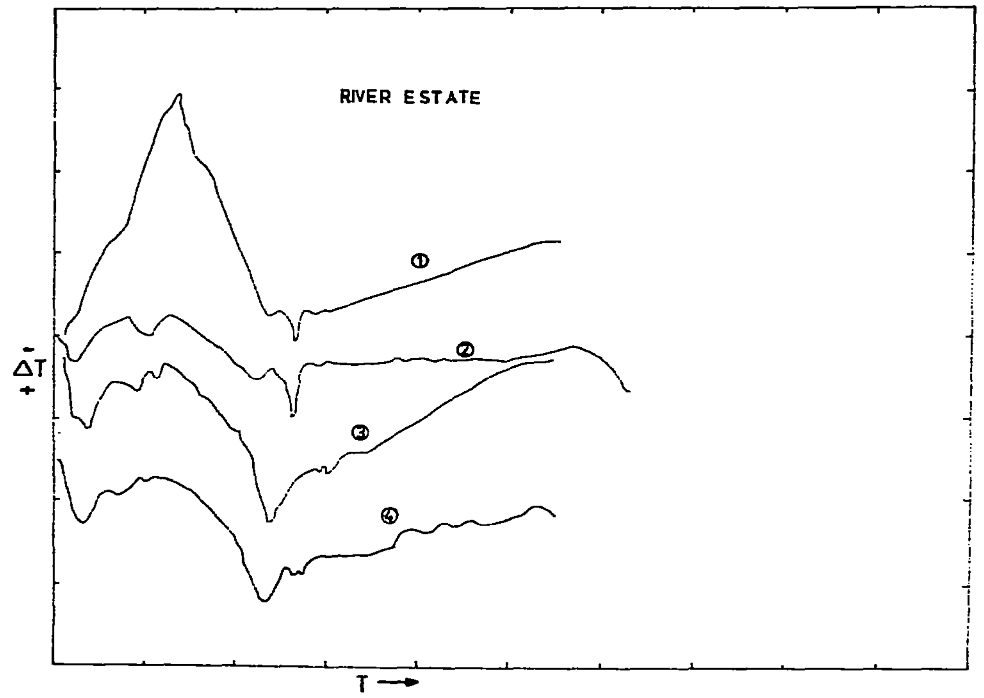

Fig. 1. DTA patterns of River Estate soil-clays.

These reaction peaks are due to the oxidation of the organic matter present in the natural soil [9]. This procedure is used to determine the relative amounts of organic matter in a soil. From the data obtained, it was concluded that Barataria peat is essentially an "organic soil". It was also observed that the replaceable cation did not significantly alter the order of the energy of the oxidation reaction (peak shape) which was initially a high energy and fast reaction followed by a second, also fast, reaction of lower energy. These reactions were followed by a third and a fourth reaction of high energies but with slower rates. The replaceable cation did, however, slightly affect the reaction temperature (initial rise of peak). It is seen that the temperature (245° C) of the first degradative oxidation reaction was identical for both samples (Fig. 2). The reaction temperatures for the second, third and fourth oxidations were lower for the magnesium saturated samples by 8, 10 and 80° C, respectively. This is believed to be due to the difference in thermal diffusivity between the "untreated" and treated soils. The Montreal clay is also rich in organic matter.

The shapes and sizes of these thermograms (Figs. 1—3) indicate the complexity of the reactions, the relative amounts of organic matter and that the mineralogy of these clays are more complex than those studied in Parts I and II [9,10]. Consequently, generalizations and groupings become more difficult. A brief discussion of the individual thermograms (only two presented) follows.

(i) The large exothermic peaks between 300 and 725° C for the analyses, performed in air, of Barataria peat [Fig. 2 (3)] overshadow the dehydroxyla-

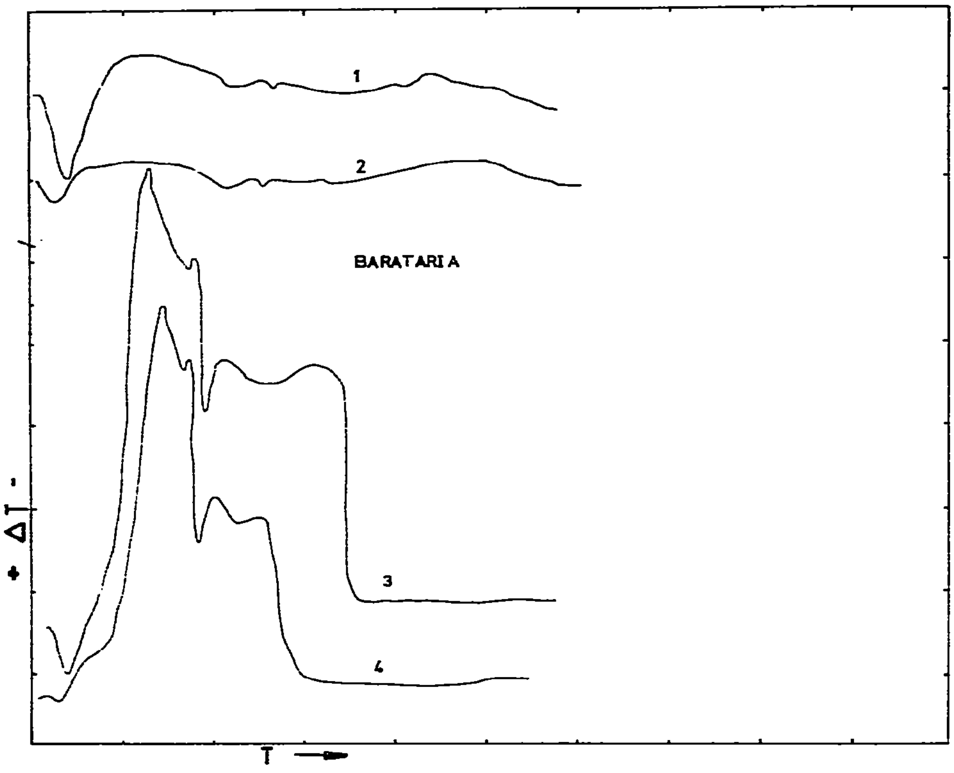

Fig. 2. DTA patterns of Barataria peat.

tion peaks at 495°C (Fig. 2: 1) and the quartz peak at 575°C. Further, no reaction is apparent at temperatures >700°C for the samples analyzed in air [Fig. 2 (3) and (4)] while there is a broad exothermic peak around 730—990°C for the untreated soil run under N_2, and at around 725—1040°C for the treated soil tested under N_2. Both the untreated and treated samples show almost identical patterns for a similar set of experimental conditions.

(ii) The untreated River Estate soil run under atmospheric conditions shows no low temperature endotherm for the removal of adsorbed water [Fig. 1 (1)] while the untreated soil tested under nitrogen [Fig. 1 (2)] shows two discrete peaks at 83 and 275°C [Fig. 1 (3)]; and in the treated sample run under nitrogen, a large double-peaked curve appeared at around 87 and 107°C, followed by a shoulder-type endotherm at 205°C, and a small endotherm at 260°C [Fig. 1 (4)].

At higher temperatures, however, the untreated samples show a small rounded endotherm followed by a sharp, almost symmetrical, endotherm at 504, 570 and 528°C for N_2 and air, respectively. Large dehydroxylation endotherms are observed at 520 and 532°C followed by a smaller endotherm at 577°C for the treated samples.

(iii) La Plaine soils all show the low temperature sorbed water endotherm at 100—107°C, the dehydroxylation endotherm at 515—545°C, and the recrystallization exotherm at 918—976°C.

The presence of impurities in the untreated soils is evident from the broad

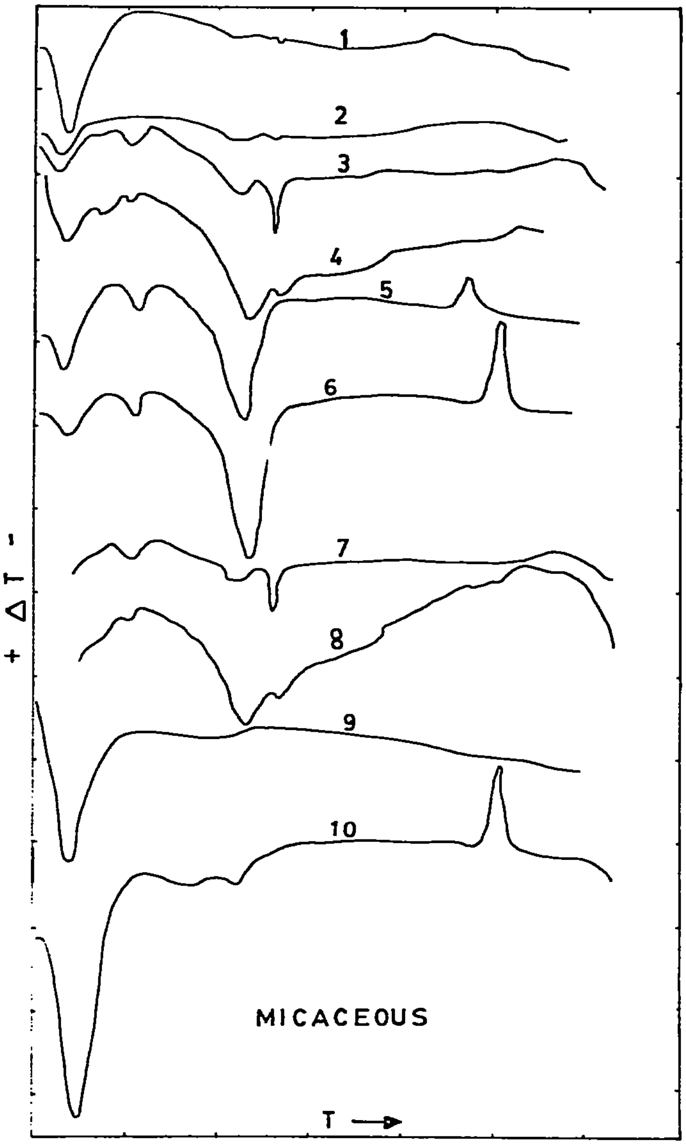

Fig. 3. DTA thermograms of some West Indian soils high in mica and organic matter.

recrystallization exotherms as compared with the sharp exotherms produced by the treated samples.

(iv) The result from the DTA study of this soil, the St. Augustine Loam, was not satisfactory. Unlike the others, triplicate results were not closely similar. The patterns illustrated in Fig. 3 (7) and (8) are those which seemed to represent the characteristic pattern based on several DTA runs.

The only samples giving a reaction peak for the release of surface moisture were the untreated soil samples run under atmospheric conditions. The others show an exothermic shift initially and only the untreated sample run under nitrogen gave an endothermic reaction peak below 500° C. Each of the patterns showed a double endothermic reaction peak between 490 and

575° C for the loss of hydroxyl water and inversion of quartz, respectively. The dehydroxylation peaks for the untreated samples are small when compared with the peaks for the same process in the treated samples or with the quartz inversion peaks in the same untreated samples. It is also observed that the 575° C peak for the inversion of quartz appeared only as a small inflection in the treated samples. A possible explanation is that the hydroxyls are much more strongly bonded in the lattice of the magnesium treated samples than they are in the untreated soil. Also, in the pretreatment of the soil considerable loss of quartz in the mechanical separation is possible.

It should be pointed out, that although the temperature for the loss of hydroxyl water varied with treatment and furnace atmosphere from 490 to 532° C, the quartz inversion temperature is essentially constant at around 573.5 ± 1.5° C. In three of the four cases the $\alpha \rightleftharpoons \beta$ quartz inversion temperature were found to be at 575° C. This result is 0.5° C lower than the findings of Stahl [11] who did extensive studies on the effects of adsorbed gases on the quartz inversion.

At higher temperatures there is a gradual exothermic shift in the treated samples, and rounded exothermic peaks for samples analyzed under nitrogen.

(v) The differential thermograms for Montreal soil all show large low temperature endotherms at 110° C and additionally at 135° C for the treated samples. These peaks are followed by the expected large exotherm between 300 and 600° C for the untreated soil run in air. The untreated sample run in nitrogen shows a rounded endotherm (435—475° C) followed by a gradual endothermic shift instead of the high temperature exothermic peak. This peak is barely visible for the untreated samples run in air, but is quite sharp for the treated samples appearing at 962 and 970° C.

In addition, the treated samples show an exothermic shift of the baseline due to slight changes in specific heat and structure as a result of the loss of moisture. The treated soil samples run under nitrogen also show an endothermic reaction peak, while an S-shaped endothermic—exothermic reaction peak is obtained for the test run in air; they appear in the temperature range 485—620° C. The thermograms of the other soils (Cunupia and Talparo) were discussed in Part II of this program [10].

Identifications

Figure 3 shows the DTA patterns of five soils (treated and untreated) run under nitrogen — the Cunupia and Talparo soil thermograms were shown in a previous paper [10]. These runs were chosen because in this procedure the interference of the organic matter is eliminated. These soils are regarded as "rich-in-mica", "organic soils", or "high-in-non-crystalline minerals". The positions and shapes of the patterns of clay mineral standards were used as the basis for identification of the soil studied in this project (Fig. 4).

Barataria peat contains essentially mica (biotite and illite) and disordered mica with traces of kaolinite, quartz and feldspar (Table 1). As can be seen from pattern of Fig. 4 (e), in the absence of expanding clays illite gives a single endothermic peak at around 107° C due to the loss of adsorbed water.

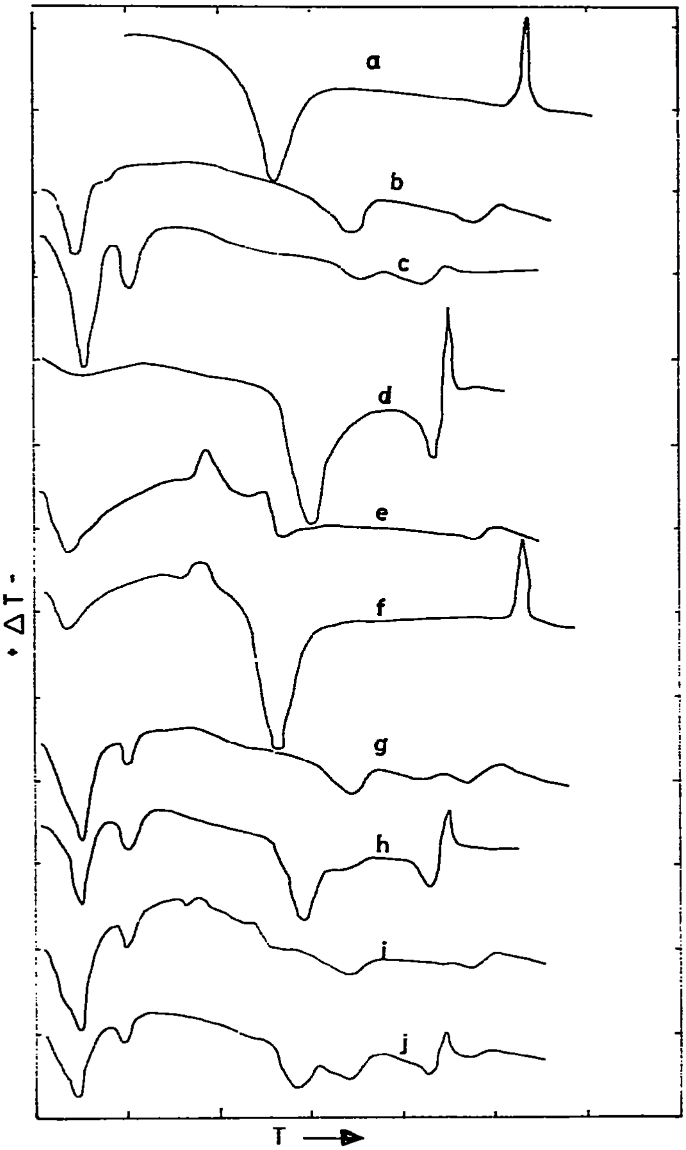

Fig. 4. DTA patterns of standard samples of clay minerals.

The DTA patterns [Fig. 3 (1) and (2)] show that there is loss of adsorbed water in this temperature range. Of greater diagnostic significance, however, are the endothermic peaks of moderate intensity due to the loss of structural hydroxyl between 500 and 600°C. These peaks are characteristic of illite and resemble the peaks in the DTA patterns of illite published by several workers in other regions. These endothermic peaks are broader than the peaks due to kaolinite which may appear in the same temperature range. When both illite and kaolinite are present the peaks between 500 and 600°C may merge [Fig. 3 (5) and (6) and Fig. 4 (f)].

The River Estate soil contains considerable amounts of illite and kaolinite together with a small quantity of interstratified chlorite—vermiculite and traces of montmorillonite and quartz. The diagnostic arguments (above) hold for this soil. In addition, however, the patterns differ significantly due to the presence of expanding clays (vermiculite and montmorillonite) and a large concentration of quartz [Fig. 3 (3) and (4)]. These result in double endothermic peaks for the loss of adsorbed water and a more pronounced quartz inversion endotherm.

La Plaine soil does not lend itself readily to broad classification. The organic content is high, but not only is the concentration of organic matter smaller than the others in this group, the concentration of kaolinite is also relatively high, and the number of clay minerals comparatively large (Table 1). This soil is classified as soil high in "mixed minerals" or "kaolinite" or "allophane". It contains illite, vermiculite and interstratified chlorite—vermiculite.

St. Augustine loam [Fig. 3 (7) and (8)] is similar to the La Plaine soil. It contains a large amount of illite and quartz as well as small quantities of kaolinite, vermiculite and chlorite (Table 1). Evidence of these small quantities was obtained from X-ray diffraction studies [12].

The Montreal clay is essentially an organic soil rich in mica (biotite). The DTA patterns [Fig. 3 (9) and (10)] show the presence of montmorillonite and kaolinite. The *d* spacings obtained from X-ray diffraction confirm the presence of these as well as the presence of feldspar and montmorillonite—vermiculite as trace minerals [12].

The Cunupia and Talparo clays are quite similar and are good examples of mixed mineralic soils (Table 1). They consist of kaolinite, montmorillonite and illite as their main clay minerals, but they also contain small quantities of montmorillonoid, goethite, and quartz. A trace of vermiculite is found in Cunupia clay.

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